August, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 2753—2762 (1988)* 2753

A Systematic Investigation of the Effects of Axial Ligands and Peripheral Substituents on the Electronic Structures of Zinc(II) Tetraphenylporphyrin π-Cation Radicals: Electrochemical EPR and Spectroscopic Observation

Kohji Ichimori, Hiroaki Ohya-Nishiguchi,* and Noboru Hirota
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

(Received February 29, 1988)

A detailed study of the effect of axial ligand and peripheral substituent on the π-system of zinc(II) tetraphenylporphyrin π-cation radical has been made using an electrochemical EPR technique. It is confirmed from the EPR spectra that most of the anions and bases examined coordinate the radicals axially. The spin density on the nitrogen nuclei in the radicals increases with the polarizability of the axial ligand estimated from the optical spectra of the parent neutral complexes. For the fourteen complexes with different substituents on the phenyl groups examined here, there is a linear correlation between the Hammett substituent constant and the spin density. It is also shown that the para position of the phenyl group carries the spin density comparable to that of the ortho position, which indicates considerable conjugation between the porphyrin ring and the phenyl groups. In most cases, there exist two kinds of radical species which give rise to broad and sharp EPR spectra at low temperature. It is suggested that the difference in the motional states of the phenyl groups in the radicals is responsible for the different EPR spectra.

The redox behavior of metalloporphyrins has been investigated widely from biological interest.[1,2] Metalloporphyrins are known to undergo two different kinds of redox reactions; the reaction of a central metal ion and of a porphyrin ring.[3] The redox properties of metalloporphyrins have been studied by making systematic variations in central metal ions,[4] peripheral substituents,[5–8] axial ligands and solvents.[9–12] Not only the metal-centered redox, but also the oxidation of a porphyrin ring are of great importance and π-cation radicals generated by the oxidation act as active species in biological systems.[13,14]

The electronic structures and characters of frontier orbitals of the π-cation radicals have been studied by means of EPR,[15,16] optical,[17,18] and MCD[19] spectroscopies combined with electrochemical techniques in addition to cyclic voltammetry.[3,17,18,20] There are two factors which influence the electronic state of the π-system: One is the axial ligand and the other is the peripheral substituent. The axial ligand are known to play important roles in the biological functions of metalloporphyrins, but their effects on the π-system have not been investigated sufficiently. The effects of peripheral substitution have been investigated in relation to basicity of free base,[21] redox potentials,[5,8,22] base addition reactions,[5,23–27] rates of metal incorporation,[28] chemical shifts,[29,30] and other physicochemical properties.[25,31–35] But their effects on the electron distribution of the π-system have not been studied directly.

Recently a systematic investigation was made on the effects of axial ligands and solvents on the π-cation radicals of 5,10,15,20-tetraphenylporphyrinatocobalt(III), $[Co(III)(tpp)]^{2+\cdot}$, in our laboratory using an electrochemical EPR technique.[36,37] It was demonstrated that axial ligands affect largely the hyperfine coupling constants (hfcc) of the nitrogen and cobalt nuclei. The changes in spin distributions caused by the axial ligands were determined directly from the analysis of the EPR spectra.

Since the zinc(II) porphyrin π-cation radicals are very stable, the techniques applied to the studies on the $[Co(III)(tpp)]^{2+\cdot}$ π-cation radical can be applied to this system as well. Moreover, zinc(II) porphyrins are free from metal-centered redox and d-π mixing in the frontier orbitals.[38] It is known that zinc(II) porphyrins can coordinate only one axial ligand.[38–42] The naturally abundant zinc nucleus carries no nuclear spin. Therefore, one can expect much simpler EPR spectra for zinc complexes than for cobalt ones. By making systematic variations of the axial ligand and peripheral substituent, their effects on the spin-density distribution of the π-cation radicals can be investigated in detail.

The EPR spectra of Zn(tpp) π-cation radical were first observed by Fajer et al., with electrochemical oxidation[43] and several works have been done subsequently.[44–47] It was shown that the π-cation radical can axially coordinate one halogen anion or one pyridine molecule,[45] but the effects of the axial ligand on the π-system have not been studied in detail. Here, we have investigated the effects of the axial ligand and peripheral substitution on the EPR spectra of the π-cation radical to see how these two factors affect the π-system.

In this paper we first describe the general feature of the EPR analysis of the zinc(II) tetraarylporphyrin π-cation radicals briefly. Second, we examine the EPR spectra of the Zn(II)(tpp) π-cation radicals obtained in the presence of various anions and bases and deduce their structures in solution. Electronic effects of the axial ligands on the π-system are also discussed. Third, the effects of the peripheral substituents on the electronic states of the Zn(tpp) π-cation radical examined are discussed by correlating the EPR parameters with the Hammett constants of the substituents. Finally the origin of the two paramagnetic species observed in most cases is discussed.

Experimental

Materials. 5,10,15,20-Tetraarylporphyrin free bases with various peripheral substituents, hereafter abbreviated as H_2(substituents on phenyl groups)(tpp), were prepared by the literature procedures[23,51,56] followed by modified purification process. In Table 1, the absorption spectra of their zinc(II) complexes are summarized together with the preparative references of free bases.

The zinc(II) complexes of these porphyrins were prepared by the method of Adler et al.[57,58] and purified by chromatography on neutral alumina with CH_2Cl_2 or $CHCl_3$ as the eluent. All synthesized zinc complexes were recrystallized from mixed solvents such as CH_2Cl_2-CH_3OH and identified by elemental analysis, TLC, and optical spectra.

CH_2Cl_2 and butyronitrile of spectroscopic grade were distilled from CaH_2 and dried over activated neutral alumina for the use of EPR measurements. Tetrabutylammonium salts (TBAX, where X=BF_4, ClO_4, NO_3, and F) were obtained by the method reported previously.[37] The preparations of dibenzo-18-crown-6 complexes with potassium salts (DB18C6-KX, where X=CN, SCN, and OAc) were carried out according to the method given by Pedersen.[59] The other reagents were commercially obtained and used without further purification.

Apparatus and Procedure. The EPR spectra were taken with JEOL PE-3X and FE-3X spectrometers equipped with a temperature controller. The π-cation radicals were generated by electrochemical one-electron oxidation of the corresponding zinc complexes using various TBA salts as electrolytes with/without bases. The applied voltages was +1.7 to +3.0 V, depending on the peripheral substituent and solvent: The voltage in n-C_3H_7CN was ca. 0.4 V higher than that in CH_2Cl_2. The procedures for the electrochemical EPR measurement and the field calibration were previously described in detail.[37,60] A Takeda Riken TR5211 frequency counter was used for measuring precise microwave frequencies. The simulation of the EPR spectra was carried out by using the literature program.[61] Absorption spectra were measured with a Shimadzu UV-2005 spectrophotometer.

Table 1. Electronic Absorption Spectra of Zinc(II) Tetraarylporphyrins[a]

Substituents	Soret	λ_{max}/nm		$\varepsilon_\alpha/\varepsilon_\beta$[b]	Preparative Ref.
		β	α		
1. 4-OCH_3	427	554	589	0.311	48,56
2. 4-$C(CH_3)_3$	426	553	592	0.268	48,49
3. 4-CH_3	426	552	592	0.270	48
4. 4-H	424	551	590	0.186	48
5. 4-F	424	551	590	0.174	48,50
6. 4-Cl	426	552	591	0.175	48,50
7. 4-$COOCH_3$	427	552	592	0.193	25,48,51
8. 4-CF_3	424	551	590	0.141	48,52
9. 4-CN	427	552	592	0.156	48
10. 2-F	423	550	584(sh)	0.086	48,50
11. 2,4,6-OCH_3	428	554	589	0.100	48,50,53
12. 3,4,5-OCH_3	429	552	593	0.192	48,54
13. 2,4,6-CH_3	424	552	589	0.097	55
14. 2,3,4,5,6-F	422	548	582	0.218	25,48

a) In C_6H_6 at 20 °C. b) Intensity ratio between the vibronic components in Q band. See Ref. 42.

Results and Discussion

EPR Analysis. The EPR spectra of zinc(II) tetraarylporphyrin π-cation radicals depended on axial ligands, peripheral substituents, and temperature. In most cases the room-temperature spectra of the Zn(tpp) π-cation radical exhibited broad nine-line structures due to four equivalent pyrrole nitrogens, indicating that the unpaired electron resides in the a_{2u} π-orbital. At sufficiently low temperatures, the spectra were often resolved further.

Using $TBAClO_4$ as a supporting electrolyte in n-C_3H_7CN, a partially resolved spectrum has been observed at −55 °C, as was reported by Fajer et al.[44] This sectrum could not be simulated without assuming superposition of two spectra; a broad nine-line spectrum identical with that observed at room temperature and a sharp spectrum resolved further by phenyl protons but with the same nitrogen coupling constant as that for the former.

In the previous works by Fajer et al. the well resolved spectra of the π-cation radical were simulated by considering the splittings due to only eight ortho-phenyl protons, because it was considered that the phenyl groups are nearly perpendicular to the mean plane of the porphyrin ring and only the ortho protons give rise to hyperfine splittings (hfs) due to the direct overlap with the unpaired electron. In our systems of the acetate-ligated and para substituted π-cation radicals, it was confirmed that the para positions carry spin densities comparable to those of the ortho positions. In the present work, therefore, 4N and 12H are assumed in the simulations of the spectra of all Zn(II)(tpp) π-cation radicals.

Dual structures of the spectra were observed in most of our systems and we succeeded in the simulation by means of the superposition of sharp and broad components. In general, the intensity of the broad component was much higher than that of the sharp one and the sharp component often disappeared at room temperature, The cause for the existence of the two paramagnetic species responsible for these two species will be discussed in the last section.

The Effects of Axial Ligands on Zn(tpp) π-Cation Radical. The axial-ligand effects on the EPR spectra were examined using the unsubstituted tpp ring. The EPR spectra were delicately influenced by the coordination of the coexisting anion or base. The results obtained from the EPR spectra are summarized in Table 2. The structures and electronic states of the radicals in solution are described in the following five parts which are classified according to the coordinating power[37] and charges of the axial ligands. The effects of the axial ligands on the electronic states of

Table 2. The EPR Parameters of Zn(tpp) π-Cation Radical with Axial Ligands

Anion or base	Solvent	T/°C	Hfcc (mT)			g	Ref.
			a_N	a_H[a)]	a_X[b)]	(±0.0002)	
ClO_4^-	$CHCl_3$		0.146			2.0025	16
	CH_2Cl_2		0.143	0.024		2.0025	16
	CH_2Cl_2		0.162	0.028			16
	DMF		0.157	0.028		2.0029	16
	C_6H_5CN		0.163	0.026		2.0026	16
	n-C_3H_7CN	25/−55	0.158	0.032		2.0025	16
Br^-	$CHCl_3$		0.160		0.818	2.0059	16
Cl^-	$CHCl_3$		0.162		0.166	2.0032	16
F^-	$CHCl_3$		0.161		0.878	2.0027	16
ClO_4^-	CH_2Cl_2	RT/−92	0.156	0.030		2.0031	This work
	n-C_3H_7CN	−44	0.158	0.029		2.0029	This work
BF_4^-	CH_2Cl_2	RT	0.155	0.030		2.0031	This work
	n-C_3H_7CN	−52	0.158	0.029		2.0029	This work
PF_6^-	CH_2Cl_2	RT/−56	0.155	0.030		2.0031	This work
NO_3^-	CH_2Cl_2	−55	0.158	0.033		2.0032	This work
F^-	CH_2Cl_2	−50	0.167	0.033	0.860	2.0031	This work
AcO^-/PF_6^-	CH_2Cl_2	−10	0.171	0.029		2.0033	This work
CN^-/PF_6^-	CH_2Cl_2	−70	0.192	0.034		2.0033	This work
SCN^-/PF_6^-	CH_2Cl_2	RT/−62	0.170	0.030	0.183	2.0033	This work
4-CNpy/PF_6^-	CH_2Cl_2	−70				2.0028	This work
4-CH_3py/PF_6^-	CH_2Cl_2	−75				2.0029	This work
$P(C_6H_5)_3/PF_6^-$	CH_2Cl_2	−60	0.176	0.032	3.284	2.0034	This work

a) In this work, a_H is determined by assuming the contribution from 12 equivalent protons otherwise noted, but 8 protons in other works. b) Hfcc due to the axial ligand.

the π-system are presented in the last part.

(1) Weak-Ligand Anions (ClO_4^-, BF_4^-, PF_6^-, and NO_3^-): When TBAX (X=ClO_4, BF_4, or PF_6) was used as a supporting electrolyte at room temperature, a nine-line spectrum was observed in both CH_2Cl_2 (Fig. 1a) and n-C_3H_7CN. The spectrum in TBAClO$_4$/CH_2Cl_2 could be simulated by assuming hyperfine coupling constants (hfcc) of 4N (0.156 mT) and unresolved 12H (0.030 mT). The hfcc of nitrogens (a_N) in the system is the smallest of all, which reflects the smallest axial perturbation. Furthermore, the change of the anions has no effect on the spectrum, indicating that the radical is free from an axial ligand. It was shown by X-ray and IR results[62)] that a perchlorate ion is bound to the radical in CH_2Cl_2 as well as in the solid state. Therefore, it is considered that the perturbation caused by the perchlorate ion is negligibly small. When cooled in CH_2Cl_2, the spectrum remained broad down to ca. −85 °C, but a partially resolved spectrum was obtained at around −94 °C (Fig. 1c).

In n-C_3H_7CN the same spectra as reported by Fajer et al., were observed with these three anions. The fact that a_N in n-C_3H_7CN (0.158 mT) is slightly larger than that in CH_2Cl_2 (see Table 2) indicates solvent ligation. The coordination of nitrile to neutral Zn(tpp) has been established from the optical spectra by Nappa and Valentine.[42)] Therefore, it is reasonable to conclude that the π-cation radical is ligated by the solvent and is not influenced by these weak anions.

When TBANO$_3$ was used as the supporting electrolyte in CH_2Cl_2, the spectrum was almost identical with that in TBAClO$_4$/n-C_3H_7CN system, indicating that the effects of a nitrate ion is similar to that of n-

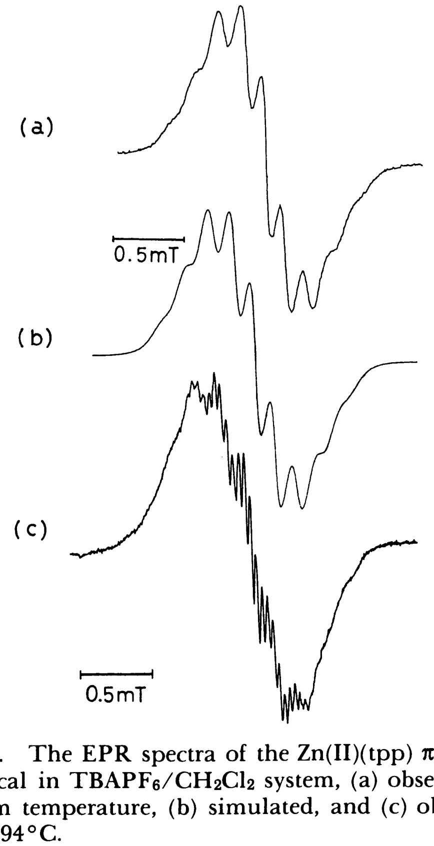

Fig. 1. The EPR spectra of the Zn(II)(tpp) π-cation radical in TBAPF$_6$/CH_2Cl_2 system, (a) observed at room temperature, (b) simulated, and (c) observed at −94°C.

C_3H_7CN.

(2) Intermediate Anions (F^-, Cl^-, and Br^-): In the presence of the halogen anions, the spectra at room temperature in CH_2Cl_2 were broad. With lowering the temperature down to −50 °C, however, the spectrum for TBAF as the supporting electrolyte showed a partially resolved structure (Fig. 2a). The spectrum could be simulated with 4N, 12H, and 1F, which means that one fluoride ion ligates to the species responsible for both the sharp and broad spectra. In simulating the spectrum, coexistence of the two paramagnetic species with the same hfcc's but different linewidth was taken into account (Fig. 2b) with the ratio of the sharp and broad components being 1 : 206. The same phenomenon was observed at lower temperatures, when TBACl was used. In the case of TBABr, however, the spectrum consisting of broad four lines due to Br^- with $I=3/2$ was not resolved further on cooling.

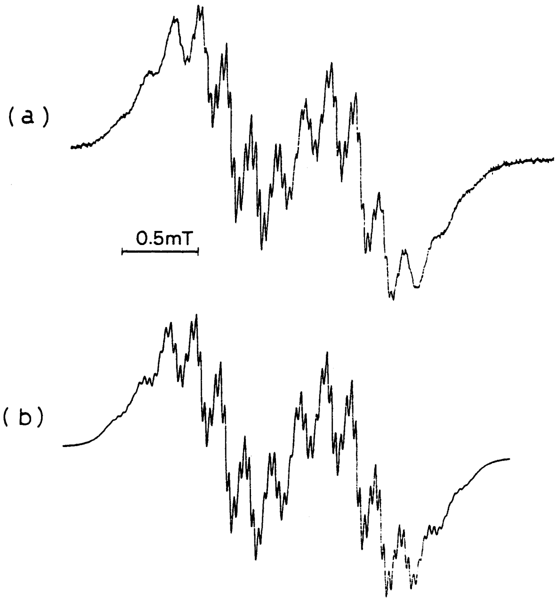

Fig. 2. The EPR spectra of the Zn(II)(tpp) π-cation radical in TBAF/CH_2Cl_2 system, (a) observed at −50 °C, and (b) simulated.

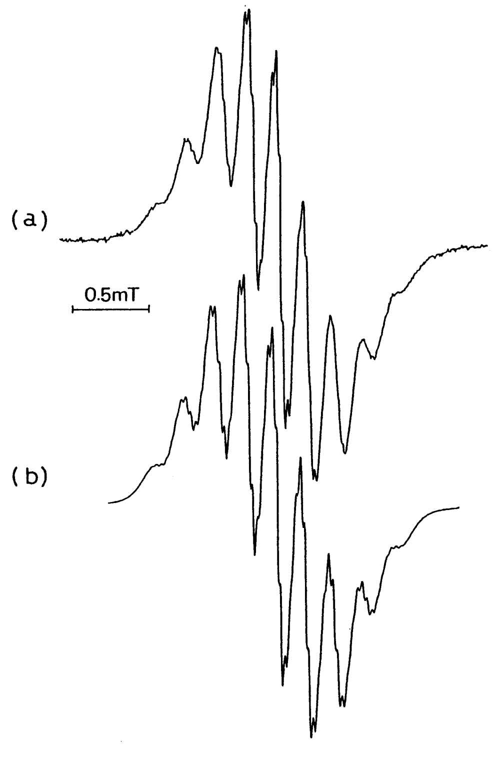

Fig. 3. The EPR spectra of the Zn(II)(tpp) π-cation radical in DB18C6-KCN(TBAPF$_6$)/CH_2Cl_2 system, (a) observed at −70 °C, and (b) simulated.

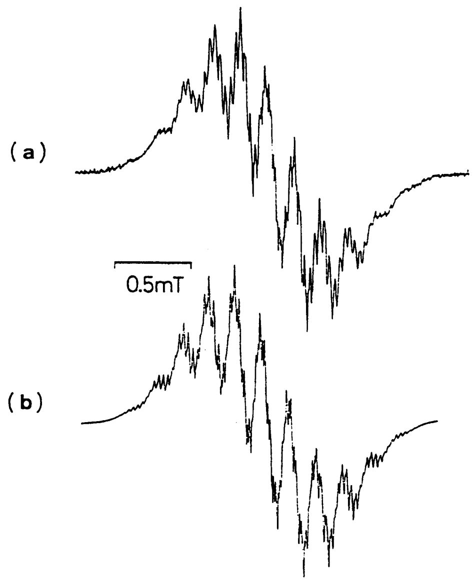

Fig. 4. The EPR spectra of the Zn(II)(tpp) π-cation radical in DB18C6-KSCN(TBAPF$_6$)/CH_2Cl_2 system, (a) observed at −62 °C, and (b) simulated.

(3) Strong Anions (CN^-, SCN^-, and AcO^-) in CH_2Cl_2: These anions were introduced in the form of DB18C6-KX complexes with TBAPF$_6$ as a supporting electrolyte as reported previously.[37] It was confirmed by the large spectral changes from the above cases (1) and (2) that these strong anions ligate the π-cation radical. The spectra in the presence of these anions also showed the dual structures at low temperatures. In the presence of cyanide, no spectrum could be observed at room temperature because of instability of the radical. But at around −70 °C, a spectrum with the largest a_N was observed, accompanied with the fine splittings due to phenyl protons (Fig. 3a). This indicates ligation by cyanide. The spectrum could be simulated by a set of 4N and 12H and assuming Sharp and Broad=1 : 289 (Fig. 3b).

In the presence of thiocyanide, a spectrum with eleven-line structure could be observed even at room temperature. This could be simulated by a set of 4N and 12H, and an additional nitrogen hfcc larger than that of the porphyrin ring. This indicates that thiocyanate ligates the π-cation radical by nitrogen, not by sulfur. At around −60 °C the spectrum was also resolved further and could also be simulated by using the same set of hfcc, as shown in Fig. 4b (Sharp: Broad=1 : 45).

The spectrum in the presence of the acetate shows much different temperature dependence. Even at room temperature, the spectrum had a dual structure which could be simulated by a set of 4N and 12H with the sharp-to-broad ratio of 1 : 130 at −10 °C. With lowering the temperature, the spectrum was once broadened but the sharp component appeared again with a more complicated structure below −55 °C. Due to the broadening on both sides of the spectrum, the simulation could not reproduce the observed spectrum well. This results from the nitrogen m_I dependence of the linewidth of the sharp component.[63]

(4) Base Ligation: Besides the anionic ligands, the electrically neutral ligands such as 4-CNpy, 4-CH_3py, and $P(C_6H_5)_3$ were also examined using $TBAPF_6$ as the electrolyte. The radical generated by the electrooxidation in the presence of these bases was unstable and the EPR spectra was not observed at room temperature. When the pyridine derivatives were used as the base, the nine-line structure described above collapsed into broad single line with slight undulation. Such broadening is probably due to the hyperfine contribution from pyridine nitrogen.

A remarkable change was seen in the spectrum, when $P(C_6H_5)_3$ was added (Fig. 5a). The central broad line was due to the unligated radical species. On both sides of the central line, a pair of nine-line spectrum was observed, which indicates clearly the ligation of one phosphine with I=1/2 in $P(C_6H_5)_3$. In n-C_3H_7CN the lines on both sides were very weak compared with the central line. Such solvent dependence of the relative intensity supports the identification mentioned above.

Extensive works about the axial ligand effects on the redox potential have been done using nitrogenous bases[17,20] and the reactions of the radical in the presence of these nucleophile have been investigated in detail.[64] The EPR spectra of $Zn(tpp)^{\ddagger}$ with axial pyridine reported by Fujita et al.[45b] show that the complex formation of the radical with pyridine results in an 10% increase in a_N. This is in accord with the trend in the anion ligation described above.

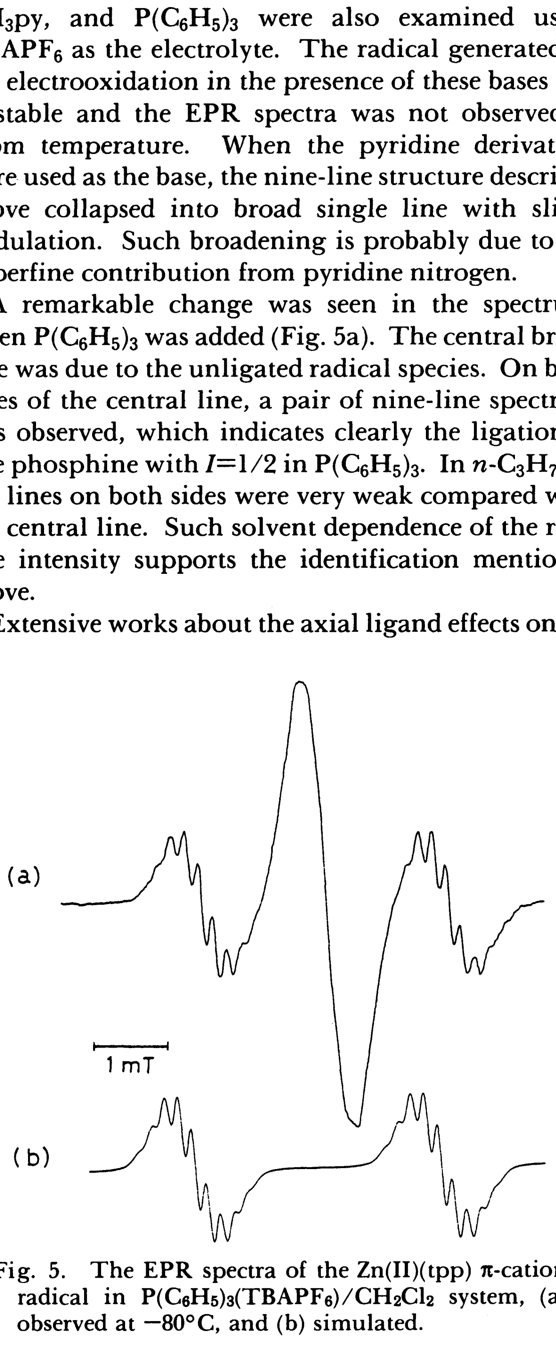

Fig. 5. The EPR spectra of the Zn(II)(tpp) π-cation radical in $P(C_6H_5)_3(TBAPF_6)/CH_2Cl_2$ system, (a) observed at −80°C, and (b) simulated.

(5) The Effect of Axial ligands on the Electronic States of the π-Cation Radical: In the previous work on the Co(III)(tpp) π-cation radical, it was noted that ligation by chloride or cyanide ion increases a_N from 0.18 mT to 0.28 mT.[37] This increase was rationalized on the bases of the result of a CNDO/2 calculation which predicts an increase of a_N with the increase of the axial ligand field. As shown in Table 2, a_N becomes larger when a strong anion coordinates to the π-cation radical. This trend qualitatively agrees with that found for the cobalt complex. However, the increase of a_N in the zinc complex is much smaller than in the cobalt one, which may be primarily due to the fewer charge of the metal cation and fewer numbers of the axial ligand.

The effects of the axial ligands on the electronic states of regular metalloporphyrins have been parametrized by means of the visible absorption spectra, which include so-called α and β bands (see Table 1).[65] In neutral Zn(tpp), considerable red shifts of these bands and the increase of the intensity ratio of α band over β band ($\varepsilon_\alpha/\varepsilon_\beta$) have been observed by introducing a wide variety of axial ligands.[42] It has been considered that $\varepsilon_\alpha/\varepsilon_\beta$ represents the electronic polarizability of the axial ligand: As more charge of the axial ligand transfers to the porphyrin ring through the metal ion, $\varepsilon_\alpha/\varepsilon_\beta$ becomes larger. We have examined the correlation between a_N and $\varepsilon_\alpha/\varepsilon_\beta$. The plot given in Fig. 6 clearly shows a correlation between these parameters except for the case of $P(C_6H_5)_3$ with neutral charge: a_N becomes larger with the increase of $\varepsilon_\alpha/\varepsilon_\beta$. It is therefore concluded that the spin density on the nitrogen nuclei increases as the polarizability of the axial ligand increases.

The Effects of Peripheral Substituents on the Zn(tpp) π-Cation Radicals. The EPR spectra of zinc-

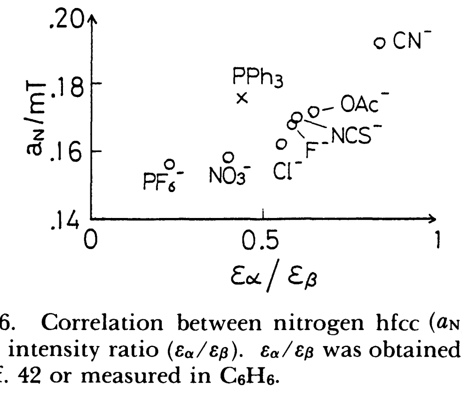

Fig. 6. Correlation between nitrogen hfcc (a_N) and the intensity ratio ($\varepsilon_\alpha/\varepsilon_\beta$). $\varepsilon_\alpha/\varepsilon_\beta$ was obtained from Ref. 42 or measured in C_6H_6.

(II) tetraarylporphyrin π-cation radicals also depended on the nature of peripheral substituents. Effects of peripheral substituents were examined with fourteen complexes by fixing the counter ion to nitrate and the solvent to CH_2Cl_2. Some typical spectra are shown in Fig. 7 to 9 and the results of the analysis are listed in Table 3.

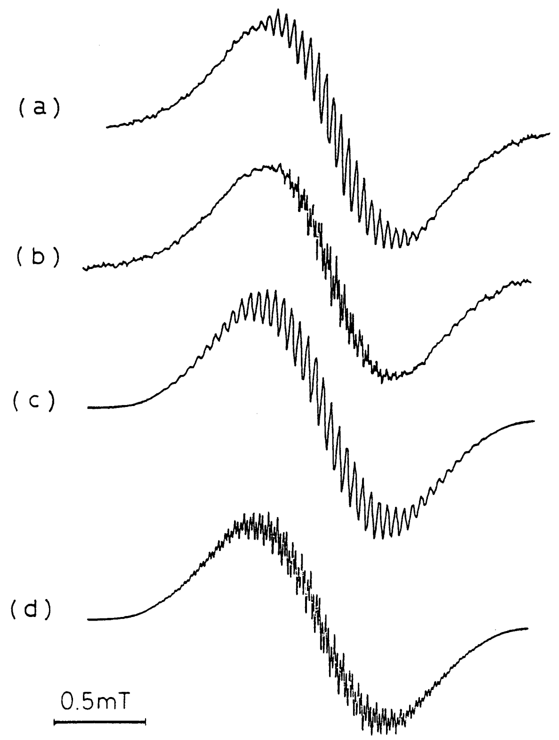

Fig. 7. The EPR spectra of the Zn(4-CH_3)(tpp) π-cation radical in $TBANO_3/CH_2Cl_2$ system, (a) observed at −60 °C and (b) observed at −80 °C. (c) and (d) are the simulated spectra corresponding to (a) and (b), respectively.

As shown in Fig. 7 and Table 3, hfs due to substituents are clearly observed in the 4-CH_3, 4-F, 4-CF_3, and 2-F complexes. This indicates that the spin density in the porphyrin ring permeates the phenyl rings and that the spin distribution can be influenced by the para substitution. This also supports our analysis which includes four para protons in simulating the spectra of the Zn(tpp) π-cation radicals.

These hfcc of the para substituents can be compared with those of the phenoxyl radical which has a_H=1.02 mT for the para proton.[66] By para substitution, a_H= 1.25 mT for 4-CH_3, a_F=2.70 mT for 4-F, and a_F=0.95 mT for 4-CF_3 have been obtained. The hfcc are amplified by factors of 1.23, 2.65, and 0.93, respectively. In the zinc complexes, the factors obtained from Table 3 are 1.33, 1.94, and 0.79, respectively. Thus the mechanism to produce the splittings due to the para substituents in both systems are quite similar. This result indicates that there is considerable conjugation between the phenyl groups and the porphyrin ring, possibly due to the wagging motion of the phenyl group. We can also conclude that the hfs of the phenyl protons are due to the spin polarization caused by the delocalized unpaired π-electron.

The dual structure mentioned in the previous section was also seen in several cases. The π-cation radicals with ortho substituents did not have sharp component. On the other hand, Zn(3,4,5-OCH_3)(tpp) π-cation radical showed a very sharp spectrum even at room temperature, as shown in Fig. 9 (Sharp : Broad= 2 : 1). The temperature at which the sharp component had the maximum intensity varied depending on the nature of substituent. These results are discussed in the last section.

Table 3. The EPR Parameters of Zn(tpp) π-Cation Radicals with Peripheral Substituents[a)]

Substituent	4σ	T/°C	Hfcc (mT)			g (±0.0002)
1. 4-OCH_3	−1.08	10	4N : 0.163	8H : 0.040		2.0032
2. 4-$C(CH_3)_3$	−0.80	−50	4N : 0.161	8H : 0.040		2.0031
3. 4-CH_3[b)]	−0.68	−80	4N : 0.158	8H : 0.033	12H : 0.044	2.0032
4. 4-H	0	−55	4N : 0.158	12H : 0.033		2.0032
5. 4-F	0.24	−16	4N : 0.156	8H : 0.029	4F : 0.064	2.0033
6. 4-Cl	0.92	0	4N : 0.158	8H : 0.028		2.0037
7. 4-$COOCH_3$	1.80	0	4N : 0.152	8H : 0.028		2.0031
8. 4-CF_3	2.16	−30	4N : 0.154	8H : 0.028	12F : 0.026	2.0030
9. 4-CN	2.64	−30	4N : 0.147	8H : 0.026		2.0032
10. 2-F		−40	4N : 0.136	8H : 0.026	4F : 0.106	2.0031
2-F[c)]		25	4N : 0.12			
11. 2,4,6-OCH_3		0	4N : 0.147			2.0028
12. 3,4,5-OCH_3	−0.12[d)]	10	4N : 0.159	8H : 0.030		2.0031
13. 2,4,6-CH_3		−20	4N : 0.160			2.0028
14. 2,3,4,5,6-F[e)]		−20				2.0027

a) In $TBANO_3/CH_2Cl_2$ system. b) 8H : 0.032 at −60 °C. c) From Ref. 16. Counterion and solvent are not described. d) σ_p=0.262 and σ_m=0.12 are assigned for OCH_3 group. Therefore, $4\sigma=4(\sigma_p+2\sigma_m)=-0.12$ can be assumed for Zn(3,4,5-OCH_3)(tpp). e) This shows a broad spectrum without splittings. The a_N may be the smallest of all because this has the smallest total linewidth.

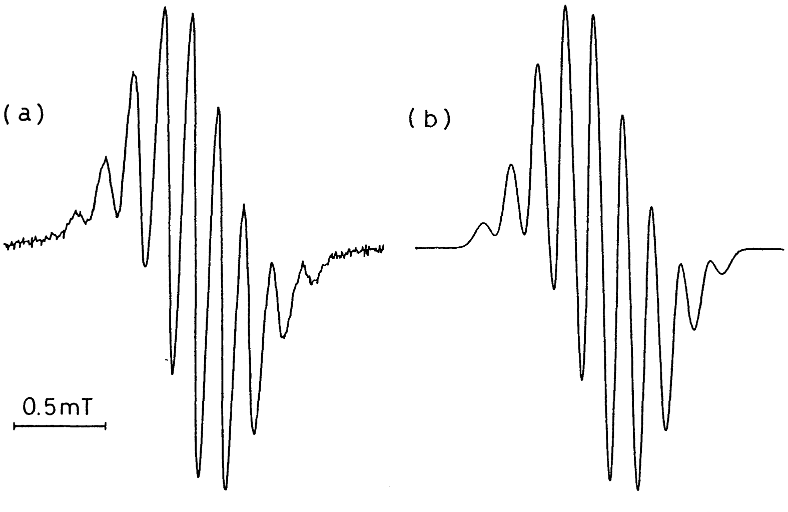

Fig. 8. The EPR spectra of Zn(2,4,6-OCH_3)(tpp) π-cation radical in $TBANO_3/CH_2Cl_2$ system, (a) observed at 0°C, and (b) simulated.

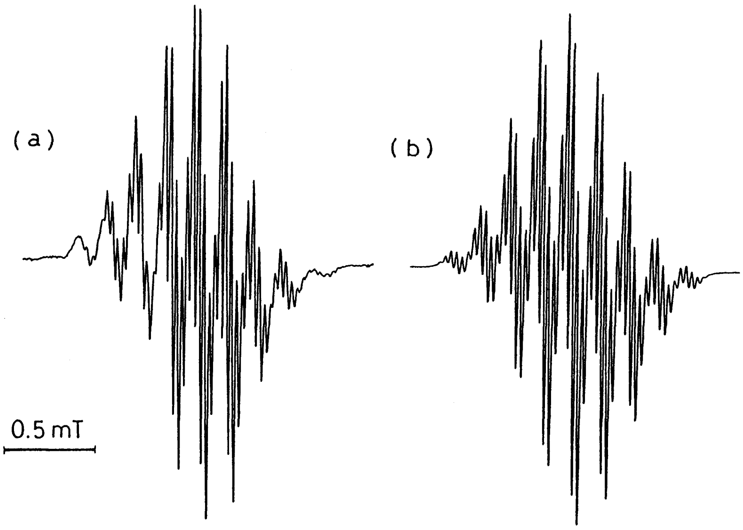

Fig. 9. The EPR spectra of Zn(3,4,5-OCH_3)(tpp) π-cation radical in $TBANO_3/CH_2Cl_2$ system (a) observed at 10°C, and (b) simulated.

The physical properties such as redox potentials and stability constants for complex formation measured in connection with the peripheral substitution have been shown to correlate with the sigma constant of the Hammett equation,[23)]

$$P = 4\sigma\rho \quad (1)$$

where P is an observed physical property, σ the Hammett substituent constant, and ρ is a proportionality constant. From the analysis of base addition reactions[23,26)] and minute NMR measurements,[29)] it has been shown that there is a significant contribution from π-induction in the transmission of the phenyl substituent effect to the whole porphyrin π-system, despite the lack of coplanarity between the porphyrin ring and phenyl groups.[67)] Thus a substantial effect may be detectable on a_N which is determined by the spin densities on the nitrogens of the π-cation radicals. The values of 4σ are listed in Table 3 together with the EPR parameters. The hfcc of a_N and a_H vs. 4σ are plotted in Fig. 10. We find considerable substituent effects on the EPR parameters and a clear Hammett linear relation between a_N and 4σ. It is seen that both a_N and a_H increase with the electron donating power of the para substituent. In the previous CNDO/2 calculations for the Co(III)(tpp)X_2 π-cation radical,[37)] it was shown that the spin densities on the meso carbons increase together with those on nitrogen as the bond length between cobalt and axial ligands are shortened. This is consistent with the observed increase of a_N and a_H, because the spin density in the phenyl groups is brought by the conjugation through the meso carbons.

From the above discussion, 2,4,6-OCH_3 and 2,4,6-CH_3 are expected to have larger a_N than 4-CH_3, But

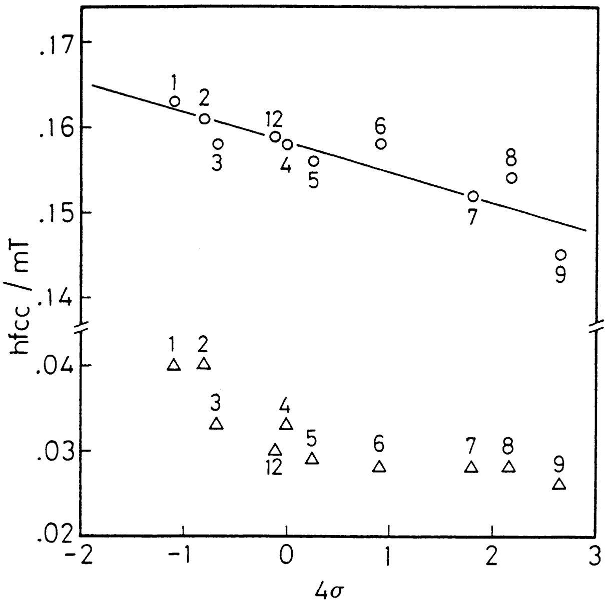

Fig. 10. Plots of a_N (O) and a_H (△) vs. Hammett constant (σ). Numbers in the figure refer to the π-cation radicals in Table 3.

2,4,6-OCH_3 and 2-F have smaller a_N values and 2,4,6-CH_3 has a comparable value compared with that of unsubstituted tpp. In these complexes the phenyl groups stand almost vertically to the porphyrin ring in so as disrupting π-conjugation. Therefore, deviations from the linear correlation between a_N and 4σ are expected in these complexes. This steric effect can also be seen in the decrease of the g-values from ca. 2.0031 to 2.0028.

Dual Structure of the Spectra. The EPR spectra of the π-cation radicals exhibit the dual structures in most cases as described above. The coexistence of the two paramagnetic species observed as the dual structure is interpreted by the equilibria between (1) the ligated and unligated radicals, (2) the radicals with different interactions with solvent, and (3) the radicals with different motional states of the phenyl groups. The most probable reason for the coexistence of two paramagnetic species is due to the change in the motional states of the phenyl groups. The ratio of the sharp and broad components is much dependent on the substituents on the phenyl groups. The π-cation radicals with ortho substituents do not have any sharp component. On the other hand, most of the other radicals exhibit substantially sharp component. Especially Zn(3,4,5-OCH_3)(tpp) π-cation radical shows the sharp component with high intensity ratio of 2 : 1 even at room temperature. Thus, it is likely that the broad component is related to the species with hindered rotations of the phenyl groups. When the rotation of the phenyl group is slow in the EPR time scale, broadening of each hyperfine line is expected because of the incomplete averaging of the unequivalent isotropic hfs as well as the anisotropic parts of hfs. The hindered rotations of the phenyl groups of the metalloporphyrins have been investigated by NMR[52,68] and the rates of the rotations and the activation energies have been determined for rutheniumcarbonyl, titanyl, indium, and gallium complexes.[34,35] These rates were indeed found to be slow in the EPR time scale. Thus it is reasonable to consider that the broad component is due to the species with hindered rotational state of the phenyl groups.

On the other hand, the sharp component in the dual structure is highly related to the free rotation of the phenyl groups. Fajer et al. have investigated the π-cation radical of Zn(II) *meso*-tetramethylporphyrin which has no sterically hindered phenyl groups,[69] and observed only the sharp component in the spectrum. It may be unlikely that the phenyl groups rotate freely. If four phenyl groups rotate cooperatively, however, apparent free rotation visualized as the sharp component becomes quite possible.

Concluding Remarks

We have investigated the effects of axial ligand and peripheral substituent on the EPR spectrum of the π-cation radical of Zn(tpp). It is shown that both the axial ligand and the peripheral substituent have large effects on the spin densities on the nitrogen atoms. The axial ligand is known to have a large effects on the behavior of the central metal ion,[33] but the present work shows that the π-system of the zinc complex is also affected by the axial ligand considerably as in the case of the cobalt complex.[37] The nitrogen hfs, a_N, is found to be sensitive to the peripheral substituent, different from the EPR[23,25] and Mössbauer[31,32] parameters of the central metal ions. A good correlation between a_N and the Hammett σ constant as well as the presence of the spin densities on the para positions indicates effective conjugation of the π-system between the porphyrin ring and the phenyl group. It is known that the energy level of the π-system is shifted by the peripheral substituents, but the present result directly shows the effect of the peripheral substitution on the π-system. It is suggested that the presence of the sharp and broad components of the EPR spectra are ascribed to the difference in the motional states of the phenyl groups.

The authors gratefully acknowledge Dr. Kiyoko Yamamoto of JEOL Co. for her kind advice to the sample preparations and kind gift of Zn(tpp) in early stage of this investigation. This work was partially supported by the Grant-in-Aid for Scientific Research on Priority Area of "Macromolecular Complexes (No. 62612005)" from the Ministry of Education, Science and Culture.

References

1) R. H. Felton, "Primary Redox Reactions of Metalloporphyrins," in "The Porphyrins," ed by D. Dolphin, Aca-

demic Press, New York (1979), Vol. 5, Chap. 3.

2) D. G. Davis, "Electrochemistry of Porphyrins," in "The Porphyrins," ed by D. Dorphin, Academic Press, New York (1979), Vol. 5, p. 127.

3) A. Worberg and J. Mannassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).

4) J. Fuhrhop, K. M. Kadish, and F. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).

5) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976).

6) K. M. Kadish and M. M. Morrison, *Inorg. Chem.*, **15**, 980 (1976).

7) K. M. Kadish, M. M. Morrison, L. A. Constant, L. Dickens, and D. G. Davis, *J. Am. Chem. Soc.*, **98**, 8387 (1976).

8) S. Ni, L. Dickens, J. Tappan, L. Constant, and D. G. Davis, *Inorg. Chem.*, **17**, 228 (1978).

9) a) K. M. Kadish and L. A. Bottomley, *Inorg. Chem.*, **19**, 832 (1980); b) L. A. Bottomley and K. M. Kadish, *Inorg. Chem.*, **20**, 1348 (1981).

10) K. M. Kadish and D. Chang, *Inorg. Chem.*, **21**, 3614 (1982).

11) S. L. Kelly and K. M. Kadish, *Inorg. Chem.*, **21**, 3621 (1982).

12) K. M. Kadish, X. Q. Lin, and B. C. Han, *Inorg. Chem.*, **26**, 4161 (1987).

13) J. Fajer, D. C. Brune, M. S. Davis, A. Forman, and L. D. Spaulding, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4956 (1975).

14) H. B. Dunford and J. S. Stillman, *Coord. Chem. Rev.*, **19**, 187 (1976).

15) J. Subramanian, "Electron Paramagnetic Resonance Spectroscopy of Porphyrins and Metalloporphyrins," in "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975), p. 576.

16) J. Fajer and M. S. Davis, "Electron Spin Resonance of Porphyrin π Cations and Anions," in "The Porphyrins," ed by D. Dorphin, Academic Press, New York (1979), Vol. 4, p. 197 and references cited therein.

17) K. M. Kadish and R. H. Rhodes, *Inorg. Chem.*, **20**, 2961 (1981).

18) E. C. Johnson, T. Niem, and D. Dolphin, *Can. J. Chem.*, **56**, 1381 (1978).

19) W. R. Browett and M. J. Stillman, *Inorg. Chim. Acta*, **49**, 69 (1981).

20) K. M. Kadish, L. R. Shiue, R. K. Rhodes, and L. A. Bottomley, *Inorg. Chem.*, **20**, 1274 (1981).

21) W. S. Caughey, W. Y. Fujimoto, and B. P. Johnson, *Biochemistry*, **5**, 3830 (1966).

22) P. Worthington, P. Hambright, R. F. X. Williams, J. Reid, C. Burnham, A. Shamin, J. Turey, D. M. Bell, R. Kirkland, R. G. Little, N. Datta-Gupta, and U. Eisner, *J. Inorg. Biochem.*, **12**, 281 (1980).

23) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).

24) F. A. Walker, M.-W. Lo, and M. T. Ree, *J. Am. Chem. Soc.*, **98**, 5552 (1976).

25) E. W. Baker, C. B. Storm, G. T. McGraw, and A. H. Corwin, *Bioinorg. Chem.*, **3**, 49 (1973).

26) G. A. McDermott and F. A. Walker, *Inorg. Chim. Acta*, **91**, 95 (1984).

27) V. L. Balke, F. A. Walker, and J. T. West, *J. Am. Chem. Soc.*, **107**, 1226 (1985).

28) J. B. Reid and P. Hambright, *Inorg. Chem.*, **16**, 968 (1977).

29) F. A. Walker, V. L. Balke, and G. A. McDermott, *Inorg. Chem.*, **21**, 3342 (1982).

30) F. A. Walker, V. L. Balke, and G. A. McDermott, *J. Am. Chem. Soc.*, **104**, 1569 (1982).

31) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4160 (1972).

32) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Am. Chem. Soc.*, **94**, 4162 (1972).

33) F. A. Walker, D. Reis, and V. L. Balke, *J. Am. Chem. Soc.*, **106**, 6888 (1984).

34) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **99**, 6594 (1977).

35) S. S. Eaton, D. M. Fishwild, and G. R. Eaton, *Inorg. Chem.*, **17**, 1542 (1978).

36) H. Ohya-Nishiguchi, M. Kohno, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **54**, 1923 (1981).

37) K. Ichimori, H. Ohya-Nishiguchi, N. Hirota, and K. Yamamoto, *Bull. Chem. Soc. Jpn.*, **58**, 623 (1985).

38) Zinc(II) porphyrins are classified into regular porphyrins: M. Gouterman, "Optical Spectra and Electronic Structure of Porphyrins and Related Rings," in "The Porphyrins," ed by D. Dolphin, Academic Press, New York (1979), Vol. 3, p. 1.

39) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).

40) C. H. Kirsley, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

41) G. C. Vogel and B. A. Beckmann, *Inorg. Chem.*, **15**, 483 (1976).

42) M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).

43) R. H. Felton, D. Dolphin, D. C. Borg, and J. Fajer, *J. Am. Chem. Soc.*, **91**, 196 (1969).

44) J. Fajer. D. C. Borg. A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **92**, 3451 (1970).

45) a) A. Forman, D. C. Borg, R. H. Felton, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 2790 (1971); b) I. Fujita, L. K. Hanson, F. A. Walker, and J. Fajer, *J. Am. Chem. Soc.*, **105**, 3296 (1983).

46) Yu. V. Glazkov, A. G. Zhurzalev, P. V. Kuzovkov, and A. M. Shul'ga, *Zh. Prikl. Spectrosk.*, **18**, 117 (1974).

47) D. Lexa and M. Reix, *J. Chim. Phys.*, **71**, 24 (1974).

48) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

49) *p*-*t*-Butylbenzaldehyde was synthesized according to the literature method: W. E. Smith, *J. Org. Chem.*, **37**, 3972 (1972).

50) J. B. Kim, J. J. Leonard, and F. R. Longo, *J. Am. Chem. Soc.*, **94**, 3986 (1972).

51) F. R. Longo, M. G. Finarelli, and J. B. Kim, *J. Heterocyclic Chem.*, **6**, 927 (1969).

52) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **97**, 3660 (1975).

53) L. Vaska, A. R. Amundsen, R. Brady, B. R. Flynn, and H. Nakai, *Finn. Chem. Lett.*, **1974**, 66.

54) R-J. Cheng, L. Latos-Grazinski, and A. L. Balch, *Inorg. Chem.*, **21**, 2412 (1982).

55) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, **105**, 6243 (1983).

56) G. H. Barnett, M. F. Hudson, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1401.

57) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J.*

Inorg. Nucl. Chem. Lett., **32**, 2443 (1970).

58) A. D. Adler, F. R. Longo, and V. Varadi, *Inorg. Synth.*, **16**, 213 (1976).

59) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

60) A. Terahara, H. Ohya-Nishiguchi, N. Hirota, and A. Oku, *J. Phys. Chem.*, **90**, 1564 (1986).

61) U. M. Oehler and E. G. Janzen, *Can. J. Chem.*, **60**, 1542 (1982).

62) L. D. Spaulding, P. G. Eller, J. A. Bertrand, and R. H. Felton, *J. Am. Chem. Soc.*, **96**, 982 (1974).

63) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper & Low, New York (1969), p. 197.

64) H. J. Shine, A. G. Padilla, and S. M. Wu, *J. Org. Chem.*, **44**, 4069 (1979).

65) M. Goutermann, F. P. Schwarz, P. D. Smith, and D. Dorphin, *J. Chem. Phys.*, **59**, 676 (1973).

66) "Landort-Boernstein," ed by H. Fischer and K.-H. Hellwege, Springer-Verlag, Berlin-Heidelberg (1979), Vol. 9, Part c2, p. 29.

67) J. L. Hoard, "Stereochemistry of Porphyrins and Metalloporphyrins," in "Porphyrins and Metalloporphyrins," ed by K. M. Smith, Elsevier, Amsterdam (1975), p. 317.

68) F. A. Walker and G. N. La Mar, *Ann. N. Y. Acad. Sci.*, **206**, 328 (1973).

69) J. Fajer, D. C. Borg, A. Forman, A. D. Adler, and V. Varedi, *J. Am. Chem. Soc.*, **96**, 1238 (1974).